Different Antioxidants on the Radiation Resistance of PP Modification Research

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Citation

Abstract
This thesis mainly studied the antioxidant 1010, antioxidant 1076, antioxidant 168 modification of PP polymer materials, through the yellow index before and after irradiation tests we can make that antioxidant 1010 and antioxidant 1076 can improve the irradiation resistance of PP; through the test of mechanical properties can be concluded that mechanical performance, though there are differences before and after irradiation, but the change is not big; Based on the thermal analysis of the sample before and after the irradiation can draw a conclusion that samples of thermal stability of slightly decreased after irradiation, crystallization temperature rise, crystallinity rise.

1. Introduction

Polypropylene is one of the fastest growing synthetic resins most widely used at home and abroad. Compared with other thermoplastic resin, PP has a number of advantages of wide source, lightweight and inexpensive, non-toxic, odorless, high strength as well as thermal and chemical stability. What is more. Isotactic polypropylene is being extensively used for the manufacture of medical supplies. [1] All medicinal products require sterilization before use. But, Discoloration is a major problem in the radiation sterilization of disposable plastic items for medical use, and be problematic in certain applications involving the curing or cross inking of polymers or resins with ionizing radiation.[2] In this paper, choosing antioxidant 1010, antioxidant 1076, antioxidant 168 as processing aid to explore the irradiation modification of PP by blending.

2. Experimental

2.1. Material

PP samples were provided by North Huajin Chemical Industries Group Company; the standard is Q/BHJ 2002-2014; the brand is T30S. Irganox 1010, Irganox 1076, Irganox 168 are from BSAF; Pure PP and various additives melt extruded and then injection molded into sample. Plastic stretch spline size is length 155mm, two wide 20mm, thickness 4mm, narrow parallel portion length of 80mm. The size of spline of the impact is 80mm×10mm×4mm.
2.2. Yellowness Test

Yellowness index is a measure of the material after irradiation important performance parameter changes, using TC-1 colorimeter measurement test, the test five samples in parallel, whichever data averages, calculated yellowness index as follows:

\[ YI = 100 \left( 1.30X_{10} - 1.15Z_{10} \right) / Y_{10} \]

\( X_{10}, Y_{10}, Z_{10} \) respectively CIE (International Commission on Illumination) 10° field of vision specified spectral tristimulus values. \( YI \) is the yellowness index. Yellowness index higher, indicating that the material is irradiated by the greater degree of influence.

2.3. Irradiation Test

The sample was placed in an electron beam irradiation apparatus irradiation, irradiation doses of 15kGy, 20kGy, 25kGy, 30kGy

2.4. Mechanics Performance Testing

Tensile strength tests and breaking elongation test were performed according to GB/T1040.1-2006 with a electronic universal testing machine (AMETEK LR30K, Britain). Five or more specimens per material were tested and the mean value of each item was determined. The testing speed was defined as 50mm/min to obtain stress-strain curves.

2.5. Scanning Electron Microscope Test

We select the flat section after finish the impact strength test to the scanning electron microscope test, the surface of the sample need to spray gold, then observe the section shape, accelerating voltage is 20 kV, collecting pictures of magnified 1000 times.

2.6. Thermal Gravimetric Analyzer (TGA) Analysis

TGA was carried out at a heating rate of 20°C/min and a gas flow of 60mL/min of \( \text{N}_2 \), samples were heated from 25°C up to 600°C with heating rate of 10°C/min.

2.7. Differential Scanning Calorimeter (DSC)

Crystallinity and crystallization temperature were determined using the differential scanning calorimeter (DSC) performed on a DSC Q500. The temperature program is from room temperature to 250°C at a rate of 20°C·min\(^{-1}\) and then from 250°C to the room temperature at a rate of 20°C, at last, from room temperature to 250°C at a rate of 10°C·min\(^{-1}\). The sample mass was 3 mg.

3. Result and Discussion

3.1. Yellowness Test Results

Square connection line shows the change of the yellowness index of pure PP under different conditions of irradiation dose, and other curves, adding different number of antioxidant 1010, under the condition of different irradiation dose, shows the yellow index changes of PP. It is that as the radiation dose increased material yellowness index increases, when the antioxidants 1010 is in 0.5, the degree of yellowness is a big fluctuation. Irradiation dose is zero, add antioxidant 1010, the yellow index decreases, this illustrate that antioxidants 1010 have an effect on the yellowness index of polypropylene. Overall, adding antioxidants in PP 1010 irradiation resistance is not good.

![Figure 1. Effect of yellowness of PP under different irradiation dose and only add antioxidant 1010.](image-url)
We all see that when adding 0.5 phr antioxidant 1076, the irradiation-resistance of the formula is better than pure PP. The yellowness of every formula is all within 2 under different irradiation dose, almost no color. In general, antioxidant 1076 on PP irradiation resistance is better. Antioxidant 1076 is a kind of typical alkyl phenolic antioxidants and it is a synthetic rubber, plastic, rubber and oil indispensable additives. Its molecules containing long chain alkyl and suitable for use at high temperature. Antioxidant 1076 can eliminate oxygen free radical which produces by PP via irradiation prevent the formation of hydrogen peroxide.

We can get that anti-yellowing ability of the material has not only increased, but more weak when adding antioxidant 168 only. With increasing radiation dose, yellowness this formula is better than pure PP. This may be caused by the antioxidant 168 has good uncompatibility with PP.

In conclusion, three kinds of antioxidants, the effect of irradiation resistant to color of antioxidant 1076 is best, adding antioxidant 1010 overall effect on yellowing is not large, while adding antioxidant 168 would result in a material yellowing degree aggrandizes.
3.2. Mechanics Performance Testing Results

By the figure can be seen, with the increase of irradiation dose, the tensile strength of the materials decreased, after adding antioxidants, the tensile strength of the material and not add antioxidants compared with varying degrees of decline, this is because the antioxidant itself may also have a certain degree of degradation by irradiation. Under 25 kGy and 30 kGy irradiation dose, the tensile strength of the formula is a little better than pure samples, it account for that under the condition of high irradiation dose, antioxidants on the material must be enhanced effect, inhibits oxidation degradation. Impact strength, with the increase of irradiation dose, the impact strength increased, antioxidant 1010 influence on impact strength without an obvious trend, but on the whole after join the impact strength of material has different degrees of improvement.
Figure 6. Effect of tensile strength of PP under different irradiation dose and only add antioxidant 1076.

Figure 7. Effect of impact strength of PP under different irradiation dose and only add antioxidant 1076.

It can be seen that with the increase of irradiation dose, the tensile strength is gradually reduce the trend. In general, the addition of antioxidant no significant influence to the change of tensile strength, and the change trend of pure PP is roughly similar. And the material with the increase of irradiation dose, the impact strength has a certain degree of improvement, but the variation is not obvious, the number of antioxidant 1076 under different irradiation dose overall is the strength of the pure PP, it can achieve the strength of the needed for daily use.
Adding antioxidant 168 in each of the irradiation dose changes under the condition of no obvious regularity, has remained at about 24-26 mpa. The impact strength of the material in more than 20 kGy irradiation dose shows varying degrees of decline.

In conclusion, with the increase of irradiation dose, the tensile strength of the PP material decreases, the impact strength decreased. Mechanical properties of high number of antioxidants 1010, 1076 of the formula is better than that of less number of the formula; antioxidants added did not cause a relatively large impact on the change of mechanical properties of materials; the overall data error within the range can be measured. And the addition of antioxidant 168 on the material impact strength has a certain degree of decline.
3.3. Scanning Electron Microscopy (SEM) Analysis

Figure 10. SEM photographs of polypropylene.

Pure polypropylene section neat, there is tiny silk on the scanning electron microscope, it belongs to the ductile fracture; When adding antioxidant 1010 and antioxidant 1076, the silk on the scanning electron microscopy images more obvious, it
can see antioxidants evenly distributed around the polypropylene and it becomes darkening, the quantity of the silk becomes fewer after irradiation. This may be antioxidant 1010 and antioxidant 1076 has a certain influence on PP color change behavior, for irradiation yellow degree we can get the test result that antioxidant 1010 and 1076 can improve the resistance to irradiation effect of PP, which is consistent with the results of scanning electron microscopy with us. Add antioxidant 168, although the radiation resistance of PP effect is not obvious, but it increased the fracture morphology of stripe, crack, presents ductile fracture.

3.4. Thermal Gravimetric Analyzer (TGA) Analysis Results

![Figure 11](image1.png)

Figure 11. Effect of antioxidant 1010 in PP TGA performance before and after irradiation.

![Figure 12](image2.png)

Figure 12. Effect of antioxidant 1076 in PP TGA performance before and after irradiation.
Pure PP thermo-gravimetric epitaxial initial decomposition temperature of 428.75°C, after adding antioxidant 1010, epitaxial starting temperature up to 432.35°C, to a certain extent, improved the thermal stability of material, adding antioxidant 1010, after irradiation, the extension initial decomposition temperature dropped to 427.17°C, thermal stability, shows that after irradiation, the electron beam energy to damage of materials within the molecular chain, reduced thermal stability. After adding antioxidant 1076, extension starting temperature drop of 402.03°C, thermal stability, after irradiation, epitaxial starting temperature up to 426.98°C. It may be that the antioxidant 1076 itself insufficient heat stability generate stable product after irradiation, the thermal stability is improved, but compared to the pure PP was slightly off. Single add antioxidant 168, extension the starting temperature of 430.05°C, fell to 427.17°C after irradiation. Although the look from the yellow degree, antioxidant 168 irradiation resistant effect is not ideal, but in front of the irradiation, the addition of antioxidant 168 make the material to improve the thermal stability of antioxidant 168 itself has good thermal stability. In general, as in the alkylation of phenol hydroxyl, registration of alkyl increased, and the branch of the substituents increased, the antioxidant efficiency increased. In neighboring, registration of benzene ring is introduced into investing electronics group, such as methyl, tertiary butyl, antioxidant effect significantly increased. While introducing electron-withdrawing groups such as aldehyde, nitrocellulose, oxidation resistance is reduced. Although antioxidants can capture and eliminate free radicals [4]. But the structure of antioxidant 1010 and 1076 is different, so they also have different antioxidant efficiency.

3.5. Differential Scanning Calorimeter (DSC) Results

![Figure 13. Effect of antioxidant 168 in PP TGA performance before and after irradiation.](image1)

![Figure 14. Effect of antioxidant 1010 in PP crystallization before and after irradiation.](image2)
Figure 15. Effect of antioxidant 1076 in PP crystallization before and after irradiation.

Figure 16. Effect of antioxidant 168 in PP crystallization before and after irradiation.

Table 1. The crystallization temperature and crystallinity before and after irradiation.

<table>
<thead>
<tr>
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<th>Crystallization temperature</th>
<th>Crystallinity</th>
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<tbody>
<tr>
<td>Pure PP</td>
<td>25.11%</td>
<td>149.15°C</td>
</tr>
<tr>
<td>Add antioxidant 1010</td>
<td>22.99%</td>
<td>152.63°C</td>
</tr>
<tr>
<td>Add antioxidant 1010 after irradiation</td>
<td>30.36%</td>
<td>160.73°C</td>
</tr>
<tr>
<td>Add antioxidant 1076</td>
<td>28.18%</td>
<td>149.62°C</td>
</tr>
<tr>
<td>Add antioxidant 1076 after irradiation</td>
<td>28.44%</td>
<td>149.13°C</td>
</tr>
<tr>
<td>Add antioxidant 168</td>
<td>27.03%</td>
<td>150.35°C</td>
</tr>
<tr>
<td>Add antioxidant 168 after irradiation</td>
<td>30.36%</td>
<td>149.55°C</td>
</tr>
</tbody>
</table>

As well-known, nucleating agent has significant effect on the crystallization behavior of polypropylene. [5] Antioxidants 1010, 1076, 168 join the PP, similar to a nucleating agent, it can improve PP crystallization temperature, degree of crystallinity and crystallization rate. The figure shows that after adding antioxidant 1010, crystallization peak position is moving in the direction of high temperature, adding antioxidants after irradiation, it continues to move high temperature crystallization peak position, it indicts that the addition of antioxidant 1010 make material increased crystallization temperature, when the material after irradiation, the crystallization temperature from 152.63°C to
160.73°C, and increased the 8°C. The crystallization area representative material crystallization enthalpy and enthalpy value can represent the material to the size of the crystallinity. Through calculation, pure PP crystallinity was 25.11%, fell to 22.99% after adding antioxidants crystallinity, crystallinity increase to 30.36% after irradiation, this is may be due to the antioxidant 1010 multiple phenol structure, stability, itself is degraded in the process of heating up, results in the decrease of crystallinity, and the structure of hindered phenol after irradiation capture material free radicals and oxygen free radicals to form stable product, it is advantageous to the heterogeneous nucleation, to a certain extent, it also have the effect of nucleation center, promote the crystallization of the material. after adding antioxidant 1076, crystallization peak position slightly move to high temperature, the change is not big, peak becomes high and narrow, it showed that the crystallization rate is increased. The addition of antioxidant 168 make the crystallization temperature of material rise slightly to 150.35°C, the crystallization temperature drop back to 149.55°C after irradiation, little change as a whole. Crystallinity increase to 27.03% after adding antioxidant 168, antioxidant 168 crystallinity was 30.36% after irradiation. The addition of nucleating agent on the crystallization structure, high-level and low-level all affect the crystalline structure, show that the addition of nucleating agent plays [6]. The addition of antioxidant also play a role of heterogeneous nucleation, so, they make crystallization temperature and the crystallinity of PP increase. The industry use of radiation in the polymer field resprents a well-established technology with multi-million dollars sales. [7] But in the medical field, there is nothing; as we all know Minoru Iwata [8] have studied the recovery of radiation-induced coloration on various polyimides; L. C. Burnea [9] have researched the radiation stability of polypropylene/lead zirconate composites; Zs. Geretovszky [10] also have discussed the photodegradation of polycarbonate under narrow band irradiation at 172 nm. A lot of people have done great research, but here are much no practical use to, so we explore them, with a view to the future into practical.

4. Conclusions

By the addition of three kinds of antioxidants on the pp yellow degree, mechanical properties, thermal analysis, etc. We can get that (1) antioxidant 1076 add 1.5 phr and 2 phr, it can have good resistance to yellowing irradiation effect, yellowing index is below 1, it basically can be regarded as no discoloration. (2) With the increase of irradiation dose, in general, no serious mechanical performance degradation, it can meet the requirements of daily products use. (3) the addition of antioxidant in PP material form the out-of-phase nucleation center, and make the crystallinity increase, after irradiation with antioxidants to form a new stable product after capture free radicals, increase the degree of heterogeneous nucleation, to further improve the crystallinity. (4) the antioxidant 1076 is insufficient, the thermal stability of PP added antioxidant 1076, material extension of initial decomposition temperature decreases, due to the formation of stable product after irradiation, up to 426°C above, it can basically meet the requirements of thermal stability, to sum up, Thermal stability is also basic requirements for daily application.

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References


